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ON THE APPLICABILITY OF DEBYE'S THEORY IN THE DETERMINATION OF THE TIME OF RELAXATION IN THE CASE OF PURE LIQUIDS

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It is well known that in the case of polar liquids the dipole moment of polar molecules cannot be determined from the polarization of the pure liquid by applying Debye's expression. The object of the present note is to point out that there is some justification in applying Debye's equation for the polarization at high-frequency oscillating field for the determination of the value of τ, the time of relaxation even in the case of pure liquids.

In the case of dilute solutions Whiffen and Thompson (1946) have taken the condition for maximum absorption as that for the maximum value of ϵ'' and the latter occurs when,

$$\omega_{max}\,\tau_0 = 1 \qquad \ldots \quad (1)$$

This is justified in the case of dilute solution, because ϵ' may be assumed to be independent of frequency, ϵ' and ϵ'' being the real and imaginary parts respectively of the complex dielectric constant ϵ^*. It is to be noted, however, that this condition for maximum absorption deduced by previous workers for solution is the condition for the occurrence of maximum value of ϵ'' and not of $\tan\delta$, and therefore, it is not applicable to pure liquids. If we want to find out the condition for maximum value of $\tan\delta$ in the case of pure liquids we find that $\tan\delta$ will be maximum when,

$$\omega\,\tau_0 = \sqrt{\frac{\epsilon_1}{\epsilon_0}} \qquad \ldots \quad (2)$$

where ϵ_1 is the dielectric constant for static field and ϵ_0 that for a field of infinite frequency.

Hence, the condition $\omega_{max}\,\tau_0 = 1$ cannot be applied in cases of pure liquids, because in such cases ϵ_1/ϵ_0 is much greater than unity and according to Eq. (2) $\omega\,\tau_0$ is greater than unity.

On the other hand, according to Debye's equation, the condition for maximum absorption is given by

$$\omega_{max}\,\tau = \frac{\epsilon_0+2}{\epsilon_1+2}\cdot\sqrt{\frac{\epsilon_1}{\epsilon_0}} \qquad \ldots\ (3)$$

Taking a typical case of benzyl chloride for which $\epsilon_0 \simeq n^2 = 2.4$ and ϵ_1 is about 8, we get from Eq. (3), $\tau = 0.792/\omega_{max}$, but from Eq. (1) we get $\tau_0 = \frac{1}{\omega_{max}}$

$$\therefore \quad \frac{\tau}{\tau_0} = 0.792$$

So, the value of τ deduced from Debye's equation is about 20% smaller than that deduced from Eq. (1). Since the radius of the rotor is proportional to $\tau^{1/3}$ this difference will not affect the radius of the rotor by more than 7%. This explains why in the case of liquids with molecules having the OH group as a substituent the radius of the rotor deduced from Debye's equation (Ghosh, 1945a, b, 1955a, b, c) was found to be appropriate for the OH group.

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